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3.231.533 SELF-CURING ACRYLIC INTERPOLYMERS Robert Y. Garrett, Avon Lake, and Gorman E. Eilbeck, Elyria, Ohio, assignors to The B. F. Goodrich Company, New York, N.Y., a corporation of New York No Drawing. Filed June 30, 1960, Ser. No. 39,787 13 Claims. (Cl. 260—29.6)

This invention relates to self-curing synthetic polymers and more particularly pertains to interpolymers contain- 10 ing units derived from a mixture comprising a lower ester of an alpha, beta-olefinically unsaturated monocarboxylic acid, an alpha, beta-olefinically unsaturated nitrile, an alpha, beta-olefinically unsaturated carboxylic acid and polymerizable carboxylic acid amide, latices of same and to the method for preparing said interpolymer and lat-

Synthetic polymers of esters of aplha, beta-olefinically unsaturated monocarboxylic acids, such as ethyl acrylate, 20 Most preferred is ethyl acrylate. are well known and have established commercial utility. The known polymers, however, are not particularly useful, per se, as coating agents, adhesives and the like. It is the usual practice to compound thermosetting resins, tackifiers and the like with the aforementioned well known synthetic polymers when they are to be used in coating and dipping applications, especially when good solvent resistance is necessary. The particular compounding formulation required for a given application may vary greatly. It would be highly desirable to obtain a single homogeneous polymeric composition which is stable for long periods of standing and can be used in numerous coating and impregnating operations to give superior products with little or no change in formulation.

Accordingly, an object of the present invention is the provision of modified synthetic polymers, primarily of the acrylate ester type, which in addition to their inherent superior heat and light aging properties also have unexpectedly good adhesive properties. Another object is the provision of novel synthetic polymers which can be readily deposited on or in a substrate material and subsequently insolubilized by moderate heating. Another object is the provision of novel, stable synthetic polymer lattices which are useful in dipping, impregnating and coating applications. Still another object is the provision of novel coated and impregnated leather, paper and nonwoven fabric articles characterized by their high strength and unexpectedly good aging properties and solvent resistance. Yet another object is the provision of a method for preparing the aforementioned novel synthetic polymers, the latices and articles coated and impregnated therewith.

The accomplishment of the foregoing and other objects will become apparent from the following description and examples, it being understood that many modifications and changes can be made in the products and processes disclosed herein by those skilled in the art without departing from the spirit and scope of this invention.

We have discovered a novel composition comprising an interpolymer composed of units derived from a polymerizable mixture of (1) from about 90 to 99.8% by weight of at least one lower alkyl ester of an alpha, betaolefinically unsaturated monocarboxylic acid, (2) from 0 to about 5% by weight of an alpha, beta-olefinically 65 unsaturated nitrile, (3) from about 0.1 to 5% by weight of an alpha, beta-olefinically unsaturated carboxylic acid and (4) from about 0.1 to 5% by weight of an N-alkylol

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amide of an alpha, beta-olefinically unsaturated carboxylic

The lower alkyl esters of aplha, beta-monoolefinically unsaturated monocarboxylic acids embodied in this invention are of the type

wherein R is a member of the class consisting of hydrogen, an alkyl radical having from 1 to 4 carbon atoms, a halogen, and a cyano group, and R' represents an alkyl radical havings from 1 to 4 carbon atoms. Representative monomers of the foregoing type are methyl acrylate, ethyl acrylate, the propyl acrylates and the butyl acrylates; an N-alkylol derivative of an olefinically unsaturated 15 methyl methacrylate, ethyl methacrylate, the propyl methacrylates and the butyl methacrylates; and methyl ethacrylate, ethyl ethacrylate, the propyl ethacrylates and the butyl ethacrylates and the like. Preferred are the monomers of the above formula wherein R is hydrogen.

The alpha, beta-olefinically unsaturated nitriles useful in the interpolymers embodied herein are preferably the monoolefinically unsaturated nitriles having from 3 to 10 carbon atoms such as acrylonitrile, methacrylonitrile, ethacrylonitrile and the like. Most preferred are acrylonitrile and methacrylonitrile.

The alpha, beta-olefinically unsaturated carboxylic acids useful in this invention are those having from 3 to 6 carbon atoms, representative members of which include acrylic acid, methacrylic acid, ethacrylic acid, mesaconic acid, citraconic acid, sorbic acid, maleic acid, crotonic acid and the like and anhydrides thereof. The preferred monomeric acids are the apha, beta-monoolefinically unsaturated carboxylic acids. The most preferred are the alha, beta-monoolefinically unsaturated monocarboxylic acids, particularly acrylic and methacrylic acids.

The N-alkylol amides of alpha, beta-olefinically unsaturated carboxylic acids embodied herein include those having from 4 to 10 carbon atoms such as N-methylol acrylamide, N-ethanol acrylamide, N-propanol acrylamide, N-methylol methacrylamide, N-ethanol methacrylamide, N-methylol maleimide, N-methylol maleamide, N-methylol maleamic acid, N-methylol maleamic acid esters, the N-alkylol amides of the vinyl aromatic acids such as N-methylol-p-vinyl benzamide, and the like and others. The preferred monomers of the N-alkylol amide type because of their ready availability and relative low cost are the N-alkylol amides of alpha, beta-monoolefinically unsaturated monocarboxylic acids and the most preferred are N-methylol acrylamide and N-methylol methacrylamide.

The preferred interpolymers embodied in the present invention are those composed of units derived from the polymerization of a mixture of (1) from about 90 to 99.8% by weight of at least one ester having the structure

wherein R is a member of the class consisting of hydrogen, an alkyl radical having from 1 to 4 carbon atoms, a halogen and a cyano group and R' represents an alkyl radical having from 1 to 4 carbon atoms, (2) from 0 to about 5% by weight of an alpha, beta-monoolefinically unsaturated nitrile, (3) from about 0.1 to 5% by weight of an alpha, beta-monoolefinically unsaturated monocarboxylic acid and (4) from about 0.1 to 5% by weight of an N-alkylol amide of an alpha, beta-olefinically unsaturated carboxylic acid having from 4 to 10 carbon atoms.